

#18212006

Masters
Thesis

193869

audi,

Aimed

EFFECTS OF SLUDGE AMENDMENTS ON SOIL CATION EXCHANGE CAPACITY,
ORGANIC MATTER, AND SUBSEQUENT HEAVY METAL UPTAKE BY VEGETABLES

by

Ahmed N. Abdi
B.S. (Eastern Michigan University) 1971

THESIS

Submitted in partial satisfaction of the requirements
for the degree of

MASTER OF ARTS

in

Environmental Biology

in the

GRADUATE SCHOOL

of

HOOD COLLEGE

December 1987

Accepted:

Thomas J. Tworowski Chairperson
Thomas J. Tworowski, Ph.D.

Gerald R. Leather
Gerald R. Leather, Ph.D.

Kathy F. Falkenstein
Kathy F. Falkenstein, Ph.D.

William A. Gray, Ph.D.
Chair, Department of Biology

Morris Teichman
Dean, Graduate School

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES	iii
ABSTRACT	iv
 Chapter	
1. INTRODUCTION	1
2. LITERATURE REVIEW.	6
Organic matter	
Cation exchange capacity	
Soil pH	
Heavy metal movement in the plant/soil environment	
3. MATERIALS AND METHODS.	17
Soil sample preparation	
Vegetable sample preparation	
Sample digestion	
4. RESULTS.	22
5. DISCUSSION	35
6. CONCLUSION	41
REFERENCES	43
APPENDIX	47

LIST OF TABLES

Table	Page
1. Cation exchange capacity of soil amended with sludge or leaf compost during four successive years.23
2. Organic matter content of soil amended with sludge or leaf compost during four successive years.23
3. Cadmium and zinc concentration in soil amended with sludge or leaf compost during four successive years.25
4. Cadmium and zinc levels in swiss chard foliage grown in sludge or leaf compost-amended soil during four successive years.26
5. Zinc levels of radish leaves and roots grown in soil amended with sludge or leaf compost during four successive years.28
6. Cadmium levels of radish leaves and roots grown in soil amended with sludge or leaf compost during four successive years.29
7. Zinc levels of beet leaves and roots grown in soil amended with sludge or leaf compost during four successive years.31
8. Cadmium levels of beet leaves and roots grown in soil amended with sludge or leaf compost during four successive years.32
9. Matrix of correlation coefficients of zinc and cadmium concentrations in vegetables vs. cation exchange capacity and organic matter in soil . .	.33

ABSTRACT

Sewage sludge compost or leaf compost was applied to garden vegetable plots at the rate of 110 metric tons/hectare per year for four consecutive years to determine the influence of soil amendments on soil cation exchange capacity and on soil organic matter. The effect of soil amendments on zinc and cadmium uptake by various species of garden vegetables was also evaluated in light of changes of these soil properties.

Sludge compost treatments increased soil cation exchange capacity, whereas leaf compost did not. In contrast, soil organic matter increased in both leaf compost and sludge compost-treated soil compared to control. Cadmium and zinc levels in soil increased following sludge treatment, but applications of leaf compost caused no significant change.

Swiss chard (Beta vulgaris L., cv. Cicla, Fordhook Giant) absorbed less zinc and cadmium from sludge compost-amended soil compared to control. Similarly, beet (Beta vulgaris, L., cv. Red Ball) leaves grown in sludge compost soil showed lower zinc and cadmium content than those grown in control plots. Metal content of leaves or roots in radish (Raphanus sativus L.) was not affected by compost-amended soil.

The results indicate that applications of leaf compost increased soil organic matter, thereby improving soil structure without increasing cadmium and zinc concentrations. Although sludge compost increased soil heavy metal concentrations, the concomitant increase in cation exchange capacity appeared to restrict metal uptake by several vegetables. Additional work is necessary to determine if sludge applications will cause heavy metal toxicity to other crops, micro-organisms, and ground water.

INTRODUCTION

Increasing population growth and urbanization has generated nearly 2415 million tons of waste per year (Tisdale et al. 1985). Nearly one-fourth of this waste originates from municipal and industrial waste-water treatment processing plants in the form of sewage sludge (Purdum and Anderson 1980). Sludge is the slurry of organic colloids, nutrients, and other contaminants resulting from the partial purification of raw waste water. Disposal requirements of such large amounts of waste have exceeded current technologies and created a need for alternative waste management capabilities (Moore 1981).

Until recently, sludge was disposed mostly by landfilling, ocean dumping, and incineration. However, legislation in the past two decades has prohibited some of these disposal techniques (Moore 1981).

The Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977 restricted disposal of sludge in landfills to prevent ground water contamination. These laws also prohibited direct dumping of sludge in offshore sites in order to prevent contamination of recreational areas and to prevent heavy metal accumulation in aquatic organisms (Squires 1983). Bioaccumulation of toxic compounds, such as heavy metals, through the aquatic food chain was thereby curtailed. Dumping of waste into the oceans had other negative aspects, such as increasing eutrophication and increasing the contamination by pathogenic organisms of aquatic ecosystems (Loehr 1981).

Incineration of sludge was similarly restricted by the Clean Air Act of 1972 because this process produced air pollution emissions that contain hydrocarbons, oxides of nitrogen and sulfur, heavy metals, carbon monoxide, and particulate matter. The high temperature (870-890°C) generated by incineration was necessary to destroy polychlorinated biphenyls, but such heat also volatilized hazardous toxic metals (e.g. mercury, arsenic, cadmium, and lead). Incineration has also increased both surface and ground water pollution from scrubber water, boiler blowdown, and the disposal of ash in landfills (Niessen 1981).

Composting is an alternative technique for the disposal of sludge. It is the conversion of biodegradable material into a usable soil conditioner (Barton 1979) by the process of aerobic microbial decomposition of organic matter. As a consequence of this metabolism, a temperature of 60°C to 70°C can be attained, ultimately inactivating some and destroying many of the pathogenic organisms in the sludge (Vesilind et al. 1976). Properly composted sludge can improve the physical and chemical properties of soil, particularly in poor soils such as strip-mined land (Moore 1981). Composted sludge is approximately 40 percent organic matter and therefore is a good soil conditioner (Jenkins 1981).

To prevent sludge from decomposing fast and giving off offensive odors, sludge is stabilized by adding lime and chlorine, and it is later heated and/or treated with radiation. Sludge stabilized by the addition of lime will also have the advantage of neutralizing acid soils and increasing the pH-dependent cation exchange capacity in the soil (Jacobs 1981).

The main objective in composting sludge is to produce an environmentally safe, humus-like material that is odorless and free of pathogens that can be used beneficially on land as a fertilizer and soil

conditioner (Parr et al. 1978). It is a source of nitrogen, phosphorus, potassium, and micronutrients, including boron, copper, iron, manganese, and zinc (Tisdale et al. 1985). The nitrogen content of composted sludge usually ranges between 1.0 to 1.5 percent. It is also a source of organic matter which significantly increases aggregate stability, water retention, and hydraulic conductivity of soil treated with compost. The addition of composted sludge also lowers bulk density and decreases surface crusting (Hornick et al. 1980). Optimum water infiltration and movement through soil is attributed to the stability of its structure (Mays et al. 1973; Hubbell and Staten 1951).

Environmental and public health concerns have restricted sludge compost application to agricultural and non-agricultural lands. Evaluations of heavy metal levels in soil are of particular concern following sludge applications. The addition of sludge to soil usually results in an increase of total soil cadmium concentration. Cadmium has been linked to human health problems, such as kidney and bone diseases, which may occur if dietary levels are increased substantially through the food chain (Anon. 1976). The maximum allowable annual application of cadmium is 2.0 kg/ha for food-chain crops and 0.5 kg/ha for leafy vegetables, root crops, and tobacco (Hornick et al. 1980).

Cadmium concentrations in sludge vary widely from 3 to 3,000 ppm (Anon. 1976). However, woodchips added to the composting process significantly dilute the metal content of composted sludge. An analysis of raw sludge from the Washington, D. C., Blue Plains Treatment Plant showed much higher zinc and cadmium levels (1780 ppm and 15 ppm respectively) than its compost (770 ppm and 5 ppm). Similar differences between raw sludge and composted sludge were obtained from Baltimore's treatment plant.

Despite the dilution effect of composting on the metal content of sludge, the process does not lower metals to within the acceptable limits for application to croplands (Parr et al. 1978). However, application limits of sludge may be increased if metal availability to plants is restricted due to ameliorating effects of sludge on soil physical and chemical properties.

Plant uptake of cadmium and zinc associated with composted sludge may introduce these metals into the food chain. However, soil properties such as organic matter, cation exchange capacity, and pH will influence cadmium and zinc uptake by plants. For example, an increased number of negative charges associated with increased soil organic matter can bind additional metals through cation exchange and through the formation of organo-metallic complexes (Logan and Chaney 1983).

Zinc and cadmium behave similarly in soils. While the amount of cadmium in circulation is about one-hundredth that of zinc, cadmium mimics zinc in roughly proportional amounts as it is adsorbed to soil surfaces and moves in the soil solution. Often, information about cadmium may be estimated by evaluating zinc. Cadmium is the heavy metal of considerable health concern, because unlike most other metals, it may be accumulated by a plant in amounts high enough to be harmful to humans and livestock without the plant showing any toxicity symptoms (Anon. 1980). Studies show that cadmium is more mobile than zinc in soil (Leeper 1978). Although plant uptake of zinc can be modulated by increasing pH, there is a limited effect of increased pH in controlling cadmium uptake by plants (Keeney et al. 1975). Unlike cadmium, zinc is a micronutrient which is required by plants in small quantities, but can be toxic to plants when a large amount of the metal is added to the soil through composted sludge. Zinc will

damage or kill plants before it accumulates in amounts dangerous to an animal that eats the plant, whereas cadmium has the ability to accumulate in a healthy plant in a concentration dangerous to an animal or human consumer without ever showing any effect in the plant (Leeper 1978).

The objective of this research was to elucidate the long-term effects of repeated compost applications on soil organic matter and cation exchange capacity and on cadmium and zinc uptake by selected vegetables. Metal uptake was studied in swiss chard (leafy vegetable) and beets and radishes (root crops). It was hypothesized that continued application of compost may increase the organic matter and the cation exchange capacity in soil, thereby offsetting the effects of adding cadmium and zinc to the soil.

CHAPTER 2

LITERATURE REVIEW

The fate of metals from sludge that has been applied to soil include passage through the medium unchanged, reaction with organic or inorganic compounds, adsorption on soil colloids, or absorption by plants (Leeper 1978). Soil properties, which may affect these reactions and processes and may subsequently influence plant uptake of metals from composted sewage sludge include organic matter, cation exchange capacity, pH, iron and aluminum oxides, texture, aeration, and moisture. Of these soil properties, organic matter, cation exchange capacity, iron and aluminum oxides, and texture tend to be relatively stable (Chaney and Giodano 1977). The mixing of sludge with soil will have complex effects because heavy metals are being added at the same time that soil properties, such as organic matter, cation exchange capacity, and pH which control heavy metal availability, may be altered.

ORGANIC MATTER (O.M.)

Organic matter is often regarded as a major factor in the sorption of metals. Soil organic matter can bind metals through cation exchange and through the formation of organo-metallic complexes (chelation) (Logan and Chaney 1983). Organic matter limits availability of micronutrients to plants as illustrated by the following: (1) organic matter extracts such as humic and fluvic acids have the ability to chelate heavy metals, (2) plant

micronutrient deficiencies are highly positively correlated with the organic matter content of soil, and (3) metal extractability increases after treating soils with H_2O_2 to destroy the organic matter (Keeney et al. 1975). For example, excessive manure applications can cause zinc deficiencies in plants (Kirkham 1977).

The largest fraction of heavy metals which combine with soil organic matter occurs in an insoluble stable combination with humic substances, such as humic acid, fluvic acid, and humin. Fluvic acid represents only 9 percent of the total organic matter in sludge, but it is essential for cadmium retention. The sorptive mechanism of cadmium by fluvic acid is probably due to the formation of salts or complexes with both carboxyl and phenolic groups. Cadmium availability to plants also decreases with increased organic matter. Haghiri (1974) found that cadmium concentrations in shoots and soil-extractable cadmium decreased with increasing cation exchange capacity.

Previous studies have demonstrated that soil organic matter levels in manure-amended soil decreased from 25mg/kg (organic matter/soil) on the first day of application to 10mg/kg after 12 days and remained constant thereafter (Miller et al. 1985). It is likely that such loss of organic matter would decrease the metal binding capacity of treated soils, resulting in increased plant uptake or ground water contamination by heavy metals. However, organic matter present in stabilized sewage sludge resists decomposition in soils (Elliott et al. 1986). The addition of composted sludge to soil, therefore, increased the organic matter content from 23 to 39 mg/kg, maintained higher organic matter levels, and prevented leaching of copper and zinc (Rappaport et al. 1987).

The rate of sludge application has been shown to have a great influence on the metal content of some plants. When an acid and a calcareous soil were amended with sewage sludge at rates ranging from zero to 180 metric tons/hectare and planted with wheat under greenhouse conditions, the solubility of zinc and cadmium in soil markedly increased under acid conditions and in proportion to the amount of sludge or metal applied. In contrast, under calcareous soil conditions their solubility was reduced which controlled their availability to the plants (Page et al. 1977).

Other studies revealed that there is a significant positive relationship between the concentration of zinc, cadmium, and copper in soybean tissue and the rate of sludge application (Williams 1983; Epstein et al. 1976). Increased heavy metal uptake occurred even though the soil cation exchange capacity increased three fold as a result of the addition of sludge and compost. Soil can bind small additions of metals considerably more strongly than large additions. As the complexing or binding sites for metals are filled, the capacity for additional binding decreases and metal availability to plants will increase (Chaney and Giodano 1977).

The formation of organo-metallic complexes influences the fate of heavy metals in soil. For example, ethylenediaminetetraacetic acid (EDTA), a synthetic chelator, significantly modified the cadmium adsorption behavior on soil (Elliott 1983). Cadmium is more readily absorbed by EDTA than by $\text{Al}(\text{OH})_3$ of the soil surface (Chubin and Street 1981). Such a metal-organic complex can be withdrawn from the soil solution in an insoluble form. Alternatively, soluble metal-organic complexes are highly mobile in the soil column (Lund et al. 1976). As a result, heavy metals such as cadmium may be more readily absorbed by plants due to chelation

(Foy et al. 1978). Generally, plants absorb elements in proportion to the elemental activity in the soil solution.

Chelating agents can increase metal activity and concentration in the soil solution and thereby enable increased metal uptake by plants (Chaney 1980). However, studies show that only a small percentage of cadmium added with sludge to soil is chelated in a soluble form (Logan and Chaney 1983). Consequently, only small quantities of metals are available for plant uptake.

At high pH, heavy metals may react in water with organic matter to form hydroxy-complexes. These metal hydroxy-complexes can combine with organic anions, forming extremely stable chelates that are adsorbed weakly to soil surfaces and are highly mobile in the soil environment. Hence, applications of effluents containing chelating agents may increase heavy metal pollution of ground water. At soil pH below 6 complexation could render cadmium less mobile. At low pH, positively-charged colloidal materials become more dominant in some soils. These surface changes may then adsorb organically-complexed cadmium and diminish the potential for plant uptake and ground water contamination (Elliott 1983; McBride et al. 1981).

CATION EXCHANGE CAPACITY (CEC)

Cation exchange capacity is a reversible chemical reaction in which cations held on the surface of soil minerals and within the crystal framework of some mineral species, plus those which are a part of certain organic compounds, can be reversibly displaced by cations of the surrounding salt solutions. The use of cation exchange capacity as a measure to predict the ability of the soil to prevent metal absorption by

crops and to limit their leaching to ground water was first adopted in England. It was used as a primary soil factor to govern metal sludge loadings based on the fact that organic matter increases the cation exchange capacity of the soil and that cation exchange capacity would increase soil metal retention (Chaney and Giodano 1977). Studies show that soil with a high cation exchange capacity is inherently safer for the disposal of waste than soil with low cation exchange capacity (Harter 1979).

Korcak and Fanning (1985) found that plants grown in soil amended with waste materials high in cation exchange capacity contained the lowest levels of metal in tissue. Haghiri (1974) also found a positive relationship between the extractable soil cadmium and the concentration of cadmium in oat shoots. He attributed the effect of the organic matter on cadmium through its cation exchange capacity property. Others (Mahler et al. 1980), however, found that cation exchange capacity was not important in determining the amount of total extractable cadmium associated with waste-amended soils in saturation extracts (available nutrients) of the soils. Haq et al. (1980) reported that the cadmium concentration of swiss chard was associated with the organic matter content of the soil but not with cation exchange capacity.

Movement of heavy metals in soil is greatly restricted when soils are amended with sludge compost. In contrast, heavy metals added to soil as metal salts quickly leach from the soil (Elliott et al. 1986). Studies of long-term sludge application on soil also indicate that there was no movement of heavy metals below the zone of sludge incorporation (Williams 1983).

Soil texture interacts with cation exchange capacity in the ability of soil to adsorb heavy metals. Various soils show that a coarse textured soil with a cation exchange capacity of five milliequivalent (m.e.) per 100g soil can hold only 5 ppm cadmium, while a fine textured soil with 15 m.e./100g soil can increase its capacity to 20 ppm cadmium. The concentration of cadmium in plants grown in sandy soil was found to be greater than those plants grown in heavier soil when soil cadmium levels are identical (Street et al. 1977). Therefore, soil texture can also be a determining factor for allowable rates of sludge application.

In a study of the effects of application rates on soil, the cation exchange capacity of the untreated soil (ranging from 5.5 to 6.4 m.e./100g) increased progressively with increasing rates of sludge and leaf compost. The increase in cation exchange capacity was greater with sludge than with compost. At the highest sludge rate (240 metric tons/hectare), cation exchange capacity increased nearly three fold and subsequently decreased. Two years following application, all treatments reflected cation exchange capacity values that were significantly higher than the control. The organic carbon content of unamended soil (1.0%) did not increase significantly following the 40 and 80 metric tons/hectare applications of either sludge or compost. However, a measurable increase to about 1.5% was noted at the 160 metric tons/hectare rate and for some treatments exceeded 2.0% at the 240 metric tons/hectare rate (Epstein et al. 1976).

SOIL pH

Soil pH shows a strong inverse relationship with metal availability for plant uptake (Anon. 1980). Heavy metals are more firmly adsorbed to

soil surfaces as pH rises from 5 to 7, because the cation exchange capacity of the organic colloids increases substantially between this pH range (Leeper 1978) . In acid soils, the colloids hold the metal loosely, increasing the opportunity for plant uptake or leaching to ground water. Logan and Chaney (1983) reported that all microelements were more soluble at low pH due to the hydrolysis of hydroxide species and the solubility of other soil phase minerals such as carbonates and phosphate. Acidity also lowers the adsorption of metals to pH-dependent specific adsorption sites on mineral surfaces and lowers the cation exchange capacity of soil organic matter.

Iron oxide binding of cadmium also increased under neutral and alkaline conditions. The capacity of soil for most hazardous inorganic substances increased under neutral and alkaline conditions (Page et al. 1977). The addition of lime to acid soils to above the neutral pH level may raise the concentration of the exchangeable calcium which would then displace some of the soil-absorbed heavy metals. Further lime applications would cause the pH to rise and lower the availability of heavy metals to plants.

Preer et al. (1983) found that the addition of hydrated lime to an acid soil reduced uptake of soil cadmium and zinc by beets, lettuce, radish, and swiss chard. The soil pH level required to effectively reduced metal uptake by plants appears to be 6.5 (Anon. 1980). Although soils are highly buffered, continuous leaching with too acid or too alkaline aqueous waste materials may alter the soil pH, thereby affecting the solubility of trace metals and the capacity of soil to attenuate them (Page et al. 1977).

Heavy metal solubility and mobility change with change in the soil pH. Such a change can affect the potential heavy metal availability and uptake

by plants (Epstein and Chaney 1978; Chaney 1982). In acid soils both cadmium and zinc are mobile (Page et al. 1977), but cadmium is relatively more mobile than zinc (Leeper 1978). Cadmium adsorption is less affected by pH in comparison with other heavy metals. It appears that because cadmium does not hydrolyze well, it does not compete effectively with other cations for sites freed by hydrolysis (Cavallaro and McBride 1980). Therefore, high pH is not as successful in minimizing cadmium availability as zinc availability (Keeney et al. 1975). Chaney and Giodano (1977) reported that zinc uptake by plants decreased linearly with increased pH. Cadmium and zinc levels in lettuce, swiss chard, and leafy vegetables from sludge compost-treated soil decreased with increasing soil pH (Anon. 1980). However, at a low pH of 5.5, zinc damage to plants was reported when excessive amounts of it were applied to soil (Leeper 1978).

HEAVY METAL MOVEMENT IN THE PLANT/SOIL ENVIRONMENT

When compost sludges are mixed into soil, chemical species of heavy metals present in the compost sludge are transformed by soil reaction such as cation exchange capacity, pH, and organisms. Metal availability to plants is controlled by the equilibrium processes of the amended soil. Metals and persistent organics are chelated and are adsorbed to soil constituents so that only very small amounts of the added metals remain soluble in the water phase of soil solution. Most of the soluble zinc, copper, etc., in soil solution are present as chelates with low molecular weight organic materials, such as fluvic acid. As a result, free metal ion activity is very low. Metals in soil solution can then move from the soil phase to the roots and be absorbed by the plant. Soluble salts and organic chelators increase ionic strength of heavy metals in soil, resulting in metal movements to the roots and uptake by plants (Chaney 1982). Albo

and Cottenie (1985) found that metal complexation with diethylenetriamine-pentaacetic acid (DTPA) reduced plant intake.

Each metal has its unique chemical and physical characteristics in soil plant systems. If the metal compounds are essentially insoluble, then that metal has a very low concentration in the soil solution and cannot be absorbed at an appreciable rate. If a metal is adsorbed or chelated very strongly by the soil, even though it is not precipitated, low plant uptake of the metal occurs. If a metal is weakly adsorbed, and not precipitated, then the metal is subject to plant uptake or leaching through the soil. Some metals (e.g. zinc, cadmium, etc.) are easily absorbed and translocated to food chain plant tissues. In contrast there are other metals (iron, lead, mercury, aluminum, etc.) which are strongly bound to soil or retained in plant roots and are not translocated to plant foliage in injurious amounts (Chaney 1982).

Other soil factors which affect cadmium and zinc availability to plants

The transfer of metals to the food chain may be restricted by what has been termed as the "Soil-plant Barrier" (Chaney 1982). These barriers include organic matter, cation exchange capacity, soil pH, and the presence of hydrous oxides of iron, aluminum, and manganese. While it is accepted that these barriers may be effective in controlling the availability of some heavy metals to plants, they appear to be ineffective in controlling cadmium availability to plants and its leaching to the environment. Under certain soil conditions, other processes such as metal-interaction, immobilization, or precipitation in the soil matrix may influence the potential environmental risk of cadmium (Chaney 1980). For example, studies showed that pronounced interactions occur between zinc and cadmium and between cadmium and calcium ions (Foy et al. 1978).

In a study of the effect of calcium and potassium on the release of cadmium from cadmium-treated koalinite and illite clays, cadmium release was much greater in the presence of calcium than potassium. Apparently higher cadmium release was related to the displacement by calcium at exchange sites (Haghiri 1976). Chaney (1973) showed decreased zinc translocation in crops was due to zinc interaction with manganese and/or zinc interaction with copper. Chaney and Giodano (1977) showed that the presence of phosphorous in the soil solution elevated zinc toxicity to crops.

In neutral and calcareous soils, the presence of increased phosphates and carbonates increase the surface adsorption properties of the soil colloids. Under these high surface charges coupled with a lower degree of hydration, cadmium becomes increasingly immobilized by chemisorption (complexation leading to surface precipitation). The resultant surface precipitation may lead to reduced cadmium availability to plants and minimize its leaching to the aquatic environment (Anon. 1980).

Plant Factors

All other factors being equal, crops can differ widely in their elemental uptake. In the same soil, spinach may contain 10 times more zinc than tall fescue, orchard grass 15 times more nickel than corn, and Swiss chard 5 times more copper than tall fescue (Chaney 1982). Swiss chard and tomato are known to accumulate metal contaminants to a greater extent than corn. Some of these differences are inherent in the metal uptake by roots; other differences may be due to soil-plant interactions. Depth and distribution of roots in the soil will also affect the likelihood of uptake (Chaney 1982). Bentgrass (Agrostis tenuis) appeared to be much less

tolerant to heavy metal contamination than perennial rye grass (Lolium perenne) (Albosel and Cottenie 1985). Cadmium "accumulator" crops include the beet family (beet, chard, spinach) and lettuce. Other crops classified by the Food and Drug Administration as leafy vegetables which are not considered exceptional cadmium accumulators in the field include collards, cabbage, turnip greens, kale, and mustard (Chaney 1982).

Zinc phytotoxicity occurs in most plants at about 500 mg zinc/kg foliage. Leafy vegetables, such as lettuce, swiss chard, and spinach, are tolerant of foliar zinc. Swiss chard does not show phytotoxicity in acid soils until foliar zinc is about 1500 mg/kg dry weight. In other plants heavy metals do not accumulate equivalently among plant organs. Cadmium movement in vegetables is greater into leaves than in fruits, grains, or tubers (Anon. 1980). Storage organs are usually only 0.5 to 0.04% as high in cadmium as the leaves of the same plants. Leafy vegetables, potatoes, and carrots are accumulators and pose greater risk to humans through the food chain than non-accumulating fruits and grains. Some leafy vegetable crops also accumulate much higher cadmium levels than do other crops grown on the same soil (Chaney 1982). Forage crops are poor accumulators of zinc compared to vegetables and crop plants (Albosel and Cottenie 1985). In order to counteract the toxic effects of heavy metal contamination, planting a non-accumulating crop is essential.

CHAPTER 3

MATERIALS AND METHODS

This thesis was developed as a result of an ongoing research project initiated in 1981 at the University of the District of Columbia, Washington, D.C. The research plots were located at Fort Reno in Northwest Washington, D. C. Six 10' x 20' plots received three treatments (2 plots/treatment) of leaf compost, sludge compost, and control. Leaf compost or sludge compost was applied in April 1982, 1983, 1984, and 1985 at a rate of 110 metric tons/hectare and mixed thoroughly with the top 10 inches of soil with a roller tiller. No applications were made to the control plots. Once each year between May and June, the plots were seeded with radish, swiss chard, and beets and the plants were allowed to grow to maturity. There were three replications of each vegetable within each plot and two complete blocks in each experiment.

Soil Sample Preparation

Two to four weeks after sowing the vegetable seeds, soil samples were randomly collected from the top 10 cm of each plot with an auger and transferred to a 160 c.c. cardboard box. Soil boxes were put in an oven for 48 hours at 50°C to dry. The dried samples were then sieved with a #35 (500 μ m) standard sieve and stored in 50 ml polyethelene centrifuge tubes.

Five grams of the soil was transferred from each tube into a beaker. Ten ml of concentrated nitric acid and 10 ml of water was dispensed into

each beaker. Beakers were swirled, covered with watchglasses, and heated to just below the simmering point at a temperature of 90°-100°C for 16 hours. The solutions were allowed to cool and later transferred into a 50 ml mixing cylinder topped with polyethylene funnels covered with filter paper (Whatman #2). Watchglasses, beakers and filter papers were thoroughly rinsed. The solutions were diluted to 50 ml volume with deionized water and mixed well. Metal analysis was conducted by atomic absorption spectrometry (Preer et al. 1987).

Vegetable Sample Preparation

At maturity (based on crop harvesting criteria), fifteen to twenty representative vegetable roots and/or leaves were randomly selected from each row within plots and placed in labelled plastic bags. Samples were thoroughly rinsed and blot dried with clean paper towels.

Fifty to eighty grams of chopped vegetable samples were transferred to an oven for 48 hours at 105°C. Beakers containing vegetable samples were cooled, weighed, and ground in a Wiley Mill to pass 20-mesh screen and stored in 15 ml plastic vials.

Sample Digestion

Vegetable samples (1.5g) from each vial was transferred into beakers. Four ml of concentrated nitric acid was dispensed into each beaker and swirled to wet samples and then 2 ml of 50 percent (1:1) sulphuric acid was added and then swirled. Several hours later the watchglasses and beakers were rinsed and the contents were heated to dryness. The beakers were removed from the hot plates and allowed to cool, and later placed in a muffle furnace and heated overnight (16 hours; 55°C). Beakers were then removed from furnace and allowed to cool. Two ml of concentrated nitric

acid and 2 ml of concentrated hydrochloric acid were dispensed into each beaker respectively, swirled and then covered with watchglasses. Contents were heated on hot plates until effervescence stopped. The watchglass and beaker walls were rinsed with a small amount of water and uncovered beakers were again heated. Beakers were removed from hot plates to cool and contents transferred to 10 ml volumetric flasks. The beakers were rinsed and the solution was diluted to volume and mixed thoroughly. Residues were allowed to settle out completely and the solution was later analyzed for metals. All soil and vegetable sample solutions were analyzed for cadmium and zinc by flame atomic absorption spectrometry (AAS) equipped with a simultaneous deuterium arc lamp background correction and electrodeless discharge lamp (EDL). All measurements were carried out using air-acetylene flame (Preer et al. 1987).

Soil samples from the vials were also analyzed for organic matter and cation exchange capacity. In the determination of cation exchange capacity, we used the summation of basic cations method and reserved acidity (Al^{3+}) method (Black 1965; Gillman et al. 1983).¹

Measurement of Basic Cations Procedure

Five grams of dry soil were placed into a 50 ml sterile polypropylene centrifuge tube and brought to 50 ml with 1.0 M ammonium chloride. The centrifuge tube was shaken for one hour in a wrist-action shaker, and centrifuged for fifteen minutes at 4750 revolutions per second. The supernatant was then filtered through Whatman #2 filter paper and 1 ml of the supernatant was pipetted into each of the three volumetric mixing cylinders. Into the first cylinder 10 ml of Lanthanum stock standard

¹James, B. R., soil chemist, Department of Agronomy. Interview by author on March 19, 1987, at the University of Maryland, College Park.

solution were added.² This first tube was used to analyze the calcium and magnesium. Into the second cylinder containing 1 ml of supernatant, 5 ml of 10,000 ppm sodium stock standard solution was added. This cylinder was used to analyze the potassium. Five ml of 10,000 ppm potassium stock standard solution was added into the third cylinder for sodium analysis. The volume in the cylinders was brought up to 50 ml with deionized water and mixed. Using the atomic absorption spectrometer, the calcium, magnesium, potassium, and sodium were analyzed. The addition of sodium and potassium stock solutions to samples is to suppress the ionization of the alkaline metals when exposed to light in the atomic absorption spectrometry. The formula used for converting the atomic absorption spectrometry reading to milliequivalent (meq)/100g soil for each element is as follows:

1. Basic cations (Mg^{+2} , Ca^{+2} , K^{+} , Na^{+})

$$\frac{\text{meq}}{100\text{g Soil}} = \frac{\frac{\text{concentration in ppm} \times \text{dilution factor}}{\text{Atomic weight of the element}}}{\text{Electron Charge}}$$

2. Acid cations (Al^{+3}) - Reserved Acidity Procedure

The supernatant from the acid digestion was also analyzed in the atomic absorption spectrometry for aluminum using N_2O acetylene and a two-inch burner head. The ppm of aluminum was used to calculate the reserved acidity according to the following formula:

$$\frac{\text{meq Al}^{3+}}{100\text{g soil}} = \frac{\text{ppm (extract)} \times \frac{\text{solution}}{\text{soil}}}{10 \times \text{equivalent weight of aluminum}}$$

3. Basic cation ($\text{Ca} + \text{Mg} + \text{K} + \text{Na}$) + Acidic cation (Al^{+3})
= Effective (total) cation exchange capacity

²Analytical Methods for Atomic Adsorption Spectrometry, 1976, Perkin-Elmer, Inc.

Organic Matter Estimation Procedure

In the determination of percent organic matter, we used the loss-on-ignition method (Nelson and Sommers 1982).³

The crucibles were dried by heating in the oven overnight until crucible weights were constant. One or two grams of dry soil samples were poured into the crucibles and dried overnight at 105°C.

Crucibles and dry soil were then moved to a desiccator to be cooled, then weighed, and transferred to a muffle furnace for 16 hours at 400°C. The crucibles and the soil were transferred to a desiccator to cool, and were later weighed. The percentage of organic matter was calculated as loss-on-ignition using the following formula:

$$100 \frac{(\text{crucible} + \text{dry soil}) - (\text{crucible} + \text{ash})}{(\text{crucible} + \text{dry soil}) - (\text{crucible})}$$

³James, B. R., soil chemist, Department of Agronomy. Interview by author on March 19, 1987, at the University of Maryland, College Park.

CHAPTER 4

RESULTS

Effect of Soil Amendments on Cation Exchange Capacity and on Organic Matter

Applications of sludge compost increased soil cation exchange capacity in 1982 and 1985 compared to either leaf compost or control (Table 1). In the sludge treatment, cation exchange capacity increased with time from 1983 to 1985. In contrast to sludge, leaf compost did not affect CEC compared to control. In 1983 and 1984, cation exchange capacity from sludge compost-treated soil was not different from either leaf compost-treated soil or control soil (Table 1).

Generally, the lowest organic matter was consistently found in control plots (Table 2). In 1982, leaf compost yielded the highest organic matter found in this study. Organic matter did not differ between sludge and leaf compost soil during the remaining years. However, in sludge compost-treated soil, organic matter showed a slight trend of increasing with time. There was no consistent pattern of change in organic matter from leaf compost plots. The high organic matter content after the 1982 treatment was followed by a decrease, an increase, and then a decrease in subsequent years.

Table 1. Cation exchange capacity of soil amended with sludge or leaf compost during four successive years.

<u>Treatment</u>	<u>1982</u> - - - - -	<u>1983</u> - - - - -	<u>1984</u> - - - - -	<u>1985</u> - - - - -
	(meq/100g)			
Sludge Compost	45 a* A	14 a C	30 a B	36 a AB
Leaf compost	23 b A	20 a A	28 a A	29 b A
Control	22 b A	32 a A	20 a A	27 b A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Table 2. Organic matter content of soil amended with sludge or leaf compost during four successive years.

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
Sludge compost	9.75 b* B	9.67 a B	12.25 a A	10.75 a AB
Leaf compost	13.75 a A	8.67 a B	11.75 a A	10.0 ab B
Control	9.25 b A	9.25 a A	9.875 b A	8.75 b A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Effects of Treatments on Level of Cadmium and Zinc in Soil

In 1982, 1983, and 1985, leaf compost did not increase soil cadmium levels compared to control (Table 3). Leaf compost treatments were associated with lower zinc levels than control in 1982, 1983, and 1985. In contrast, the sludge compost increased soil cadmium and zinc levels during 1982, 1984, and 1985. There was no difference in cadmium levels between treatments in 1983. The lowest level of metals was also recorded for 1983. The highest level of soil cadmium was recorded for 1984.

From 1982 to 1984, neither cadmium nor zinc appeared to accumulate in soil treated with either type of compost. For example, cadmium levels of 0.82 ppm were found in 1982 following sludge-compost treatments. In 1983, cadmium levels decreased to 0.16 ppm indicating no residual cadmium buildup. In addition, there appears to be great variability in heavy metal concentration from year to year. There was a rhythmic pattern of change in soil metal levels for all treatments among years. Metal levels decreased in 1983, increased in 1984, then decreased in 1985.

Effects of Treatments on Plant Uptake of Cadmium and Zinc

The least zinc and cadmium content of swiss chard was consistently associated with sludge compost (Table 4). Zinc and cadmium levels in swiss chard were similar following leaf compost or control treatments. Plants grown in control plots occasionally had greater heavy metal content than either compost treatment. The highest zinc and cadmium content of swiss chard was recorded in 1985. Zinc and cadmium content of swiss chard in both compost treatments decreased in 1983 compared to 1982. There was no change in zinc content of swiss chard between 1983 and 1984. In contrast,

Table 3. Cadmium and zinc concentration in soil amended with sludge or leaf compost during four successive years.

<u>Cadmium in Soil</u>				
<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.82 a* C	0.16 a D	1.35 a A	0.90 a B
Leaf compost	0.31 b C	0.13 a D	0.72 b A	0.45 b B
Control	0.32 b B	0.20 a C	0.58 c A	0.43 b B

<u>Zinc in Soil</u>				
<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	197.67 a B	101.3 b D	236.7 a A	186.3 a C
Leaf compost	143.8 b A	120.0 b C	150.8 b A	132.5 c B
Control	176.3 a A	131.3 a C	145.8 b B	138.8 b C

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Table 4. Cadmium and zinc levels in swiss chard foliage grown in sludge or leaf compost-amended soil during four successive years.

Zinc in Swiss Chard

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	99.14 c* B	73.3 c C	80.6 b C	239.0 b A
Leaf compost	307.7 a A	170.0 b B	158.3 a B	336.7 a A
Control	189.3 b B	200.5 a B	157.8 a C	311.1 a A

Cadmium in Swiss Chard

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.83 c B	0.24 c D	0.57 b C	2.08 b A
Leaf compost	1.45 a B	0.41 b D	1.18 a C	2.80 a A
Control	1.12 b B	0.60 a C	1.01 a B	2.78 a A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

cadmium content of swiss chard progressively increased from 1983 through 1985 for both treatments and control.

In 1982, 1984, and 1985, zinc content of radish leaves grown in sludge compost was lower compared with leaf compost and control (Table 5). Zinc content of radish leaves from sludge compost was lower than leaf compost. Generally, there was no difference in zinc content of radish roots between sludge compost and leaf compost. Zinc content of radish roots from control plots was higher compared to either compost treatments from 1982 through 1984. Zinc content in radish leaves and roots grown in sludge compost increased with time. While there was no pattern of change in zinc content of radish leaves grown in leaf compost-treated soil, zinc content of radish roots showed an increase with time. Generally, zinc content of radish plants from control plots increased with time.

There was no appreciable change in cadmium level in radish leaves between treatments or through time (Table 6). In 1982 and 1983, there was no difference of cadmium content of radish leaves grown in sludge compost-treated soil compared with control. However, in 1984 and 1985, cadmium content of radish leaves from either treatments were lower compared with control. There was no difference in cadmium content of radish leaves between treatments. Cadmium content in radish leaves from plants grown in sludge compost-treated soil did not change with time. Cadmium content of radish roots from sludge compost-treated soil did not differ from cadmium content of radish roots from control soil. There was no consistent pattern of change in cadmium content of radish roots with time. The highest cadmium content of radish roots for both treatments and control was found in 1985.

Table 5. Zinc levels of radish leaves and roots grown in soil amended with sludge or leaf compost during four successive years.

Zinc in Radish Leaves

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	37.9 c* C	56.1 a B	88.9 c A	38.9 c C
Leaf compost	68.5 a B	51.3 b C	95.0 b A	59.4 a B
Control	55.4 b C	60.6 a B	103.9 a A	47.8 b D

Zinc in Radish Roots

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	20.3 b D	51.0 b C	87.2 b B	92.7 a A
Leaf compost	23.0 a D	51.0 b C	87.8 b B	103.0 a A
Control	24.0 a C	55.0 a B	92.0 a A	86.0 a A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Table 6. Cadmium levels of radish leaves and roots grown in soil amended with sludge or leaf compost during four successive years.

Cadmium in Radish Leaves

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.30 b* A	0.24 a A	0.30 b A	0.30 b A
Leaf compost	0.40 a A	0.14 b C	0.30 b B	0.30 b B
Control	0.30 b B	0.20 ab C	0.40 a A	0.40 a A

Cadmium in Radish Roots

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.09 b C	0.24 a B	0.02 b D	0.50 a A
Leaf compost	0.20 a B	0.09 b C	0.12 a C	0.50 a A
Control	0.08 b D	0.30 a B	0.14 a C	0.50 a A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

In 1984 and 1985, beet roots had greater zinc concentration following leaf compost than sludge compost treatment or control (Table 7). However, the foliage of beets showed generally lower zinc content in sludge compared to leaf compost or control in 1982, 1983, and 1984. Beet leaves and roots showed a substantial increase in metals in 1983. Beet leaves and roots from either compost treatment or control generally decreased zinc content after 1983. Zinc content of beet roots from leaf compost treatment was generally higher than zinc content of beet roots grown in sludge compost-treated soil and control. Beet roots from sludge compost-treated soil contained the least zinc compared to leaf compost and control.

Cadmium content in beet leaves was lower for sludge compost-treated soil compared to leaf compost-treated soil and control for all years (Table 8). Cadmium content of beet leaves grown in sludge compost-treated soil was consistently lower compared with leaf compost soil and control plants. For 1983, 1984, and 1985 cadmium content of beet leaves grown in leaf compost soil did not differ from control plants. For 1982, 1983, and 1984, cadmium content in beet roots grown in sludge compost was also lower compared with leaf compost plants. In 1982 and 1983, cadmium content in beet roots grown in sludge compost-treated soil did not differ compared with control plants.

Generally cation exchange capacity and organic matter were better correlated with plant metal content in beets than in swiss chard or radish (Table 9). In beets, a decrease in metals was associated with an increase in soil organic matter. However, the relationship between tissue metal content and soil cation exchange capacity was not well defined.

Table 7. Zinc levels of beet leaves and roots grown in soil amended with sludge or leaf compost during four successive years.

Zinc in Beet Leaves

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	96.1 c* B	400.0 c A	61.1 b C	64.3 b C
Leaf compost	258.7 a B	710.0 a A	106.1 a D	132.2 a C
Control	141.7 b B	750.0 a A	124.5 a B	62.2 b C

Zinc in Beet Roots

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	52.8 c B	366.0 b A	56.7 c B	41.1 b C
Leaf compost	82.0 a B	446.7 a A	75.6 a B	51.7 a C
Control	59.3 b B	420.0 a A	63.3 b B	42.2 b C

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Table 8. Cadmium levels of beet leaves and roots grown in soil amended with sludge or leaf compost during four successive years.

Cadmium in Beet Leaves

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.70 c* C	3.6 b A	0.83 b B	0.44 b D
Leaf compost	1.40 a B	3.93 ab A	1.12 a C	0.72 a D
Control	0.94 b B	4.3 a A	1.08 a B	0.76 a C

Cadmium in Beet Roots

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (ppm) - - - - -			
Sludge compost	0.24 b D	1.50 b A	0.40 b C	0.60 a B
Leaf compost	0.30 a C	1.87 a A	0.52 a B	0.23 c D
Control	0.21 b D	1.60 b A	0.50 a B	0.30 b C

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row.

Table 9. Matrix of correlation coefficients of zinc and cadmium concentrations in vegetables vs. cation exchange capacity and organic matter in soil. *

SLUDGE COMPOST

Plants	Plant Zinc		Plant Cadmium	
	CEC	O.M.	CEC	O.M.
Swiss chard	+ 0.54	- 0.02	+ 0.61	- 0.04
Beet leaf	- 0.66	- 0.63	- 0.80	- 0.50
Beet root	+ 0.74	- 0.65	- 0.50	- 0.60
Radish leaf	- 0.21	+ 0.50	+ 0.43	+ 0.24
Radish root	+ 0.40	+ 0.30	- 0.10	- 0.42

LEAF COMPOST

Plants	Plant Zinc		Plant Cadmium	
	CEC	O.M.	CEC	O.M.
Swiss chard	+ 0.12	- 0.04	+ 0.30	+ 0.60
Beet leaf	- 0.73	- 0.62	- 0.60	- 0.34
Beet root	- 0.78	- 0.68	----	----
Radish leaf	- 0.94	+ 0.40	+ 0.71	+ 0.60
Radish root	+ 0.50	----	----	----

CONTROL

Plants	Plant Zinc		Plant Cadmium	
	CEC	O.M.	CEC	O.M.
Swiss chard	+ 0.10	- 0.20	- 0.60	- 0.24
Beet leaf	+ 0.60	- 0.10	+ 0.41	- 0.02
Beet root	+ 0.52	- 0.11	+ 0.41	- 0.18
Radish leaf	- 0.32	+ 0.33	- 0.30	- 0.30
Radish root	- 0.30	+ 0.44	- 0.30	- 0.40

* Negative (-) number indicates that as cation exchange capacity or organic matter increased, plant metal uptake decreased. Positive (+) number indicates that as cation exchange capacity or organic matter increased, plant metal uptake increased.

The increase in cadmium and zinc uptake in 1985 (Table 4) corresponds to a decrease in organic matter in 1985 (Table 2). The correlation matrix showed that there was a strong negative correlation between soil cation exchange capacity and radish leaf content of cadmium and zinc (Table 9). Tissue zinc content of beet leaves and roots were well correlated with cation exchange capacity and organic matter in both sludge compost and leaf compost treatments. As organic matter and cation exchange capacity increased, zinc plant uptake decreased.

CHAPTER 5

DISCUSSION

There was a general increase of organic matter and cation exchange capacity in sludge compost plots and to some extent in the leaf compost plots, while the controls showed no change. The sludge treatment in 1982 (Table 2) did not cause an increase in either organic matter or cation exchange capacity of the soil. It is possible that due to delays in humification there was a lag time between compost application and any appreciable change in soil organic matter and cation exchange capacity. Sludge applied to land must be decomposed to colloidal size before an appreciable increase of cation exchange capacity in the soil is achieved. Decomposition of organic matter is dependent on environmental parameters such as temperature, moisture, soil pH, and the presence of microbes in soil system. Variability of these parameters could have caused some of the differences in the quantity of organic matter decomposed. For instance, the amount of rainfall during the 1983 planting season was unusually low in Washington, D. C. A decrease in soil moisture could restrict the activities of soil organisms and could account for the unusual high levels of cadmium and zinc in 1983 (Table 7 and 8). Studies show the microbial activities may also control the movement and availability of metals in the added sludge compost. For instance, the rate of phosphorus and sulphur immobilization and mineralization in sludge compost-treated soil is determined by microbial activities (Hinesly et al. 1977).

Composted sludge will increase soil organic matter and cation exchange capacity (Hornick et al. 1980), but will require massive amounts to achieve only a small increase in soil organic matter (Kirkham 1977). Increases in organic matter have been observed years after sludge compost treatment (Page et al. 1977). This study also showed an increase of organic matter with time. The low level of organic matter and cation exchange capacity reported for 1983 (Table 1) may have resulted from the low rainfall reported for that season which may have reduced the microbial activities in the soil. The volatilization of soil organic carbon is also possibly due to microbial degradation of sludge compost. Organic carbon may reach an equilibrium between amounts applied on sludge compost-treated plots and amounts lost by volatilization each year (Hinesly et al. 1977) .

At the rate and duration of compost application that was used, there was not a general and pronounced effect on soil organic matter and cation exchange capacity (Table 3). In another study, increasing the rate of application caused a significant increase of organic carbon in the soil (Epstein et al. 1976). In the current study, higher applications of sludge compost were unacceptable due to cadmium and zinc concentrations.

Where cation exchange capacity values for the sludge-composted soils were relatively high, the metal uptake was reduced effectively (Table 4). Cadmium levels in soils treated with sludge compost were higher than cadmium levels in soils from leaf compost and control plots (Table 3). However, cadmium levels in plants from the sludge compost treatments were substantially lower, which may emphasize the significance of the organic matter and cation exchange capacity. Haghiri (1974) reported that the cadmium concentration in oat shoots decreased with increasing cation

exchange capacity of the soil. High organic matter and high soil pH both reduce metal uptake (Page et al. 1987). Our sludge compost had a relatively high pH (Preer et al. 1984) compared to leaf compost and control.

The physical nature of leaf compost often produced clumps which were difficult to separate and hindered the decomposition process. This created a potential for an uneven distribution and mixing of the leaf compost in the soil, resulting in areas of unusually high or low organic matter content which may have biased the sampling and yielded the high organic matter estimate of 1982.

Since composted sludge contains cadmium, a yearly application would likely increase both soil cadmium and plant cadmium; however, no such increase is observed. In fact the available cadmium level in soil decreased in 1985 compared to the previous years. This may have been due to the effect of organic matter and cation exchange capacity (Street et al. 1977) which had increased as a result of sludge compost application through the years. Organic matter can bind heavy metals through increased cation exchange capacity and through chelation. Where sludge is continuously applied as on dedicated sites, the sludge organic matter acts as a retainer for cadmium. However, when the sludge applications have ceased, cadmium may be released to plants or to ground water as the organic matter undergoes decomposition.

More zinc and cadmium were found in beet leaves and radish leaves than in beet roots and radish roots (Tables 7 and 8). Crops differed in cadmium uptake by roots, and also differed in the fraction of cadmium translocated to shoots (Page et al. 1987). Others have reported that cadmium accumulation by vegetable tissues is greater in leaves than in fruits,

grains, and tubers of plants (Anon. 1980). These differences may be related to plant difference and/or metal activities. For instance, when corn is grown on soils amended with cadmium, slightly higher increases of cadmium are found in the corn leaves, while lower accumulations are found in the corn grain (Anon. 1980). Our study showed similar foliar difference. Zinc and cadmium content of beet leaves were higher compared to beet roots in either compost-treated soils and control (Tables 7 and 8).

Species differences were also observed. While zinc and cadmium content of swiss chard from sludge compost was low, neither compost treatments affected the metal levels of radish leaves or roots. Radish leaves and roots absorbed less zinc and cadmium than beet leaves and beet roots (Tables 5 and 6). Chaney (1982) reported a similar difference. Cadmium and zinc can be increased in edible crop tissues when sewage sludges rich in the elements are applied to acidic soils. Some variation in relative increased heavy metal concentration among crops may result from high soil organic matter or from calcareous vs acidic soil conditions (Page et al. 1987). The lack of correlation between cation exchange capacity, organic matter, zinc, and cadmium in some vegetables could be related to several uncontrolled environmental variables, such as temperature, rainfall, microbial activities, inherent in most field studies. A sprinkler system would have been useful to control the watering and ensure even distribution of metals dissolved in soil solution to the plants.

Unlike leaf compost, sludge compost was limed as part of the routine composting process. As a result, the pH-dependent cation exchange capacity of leaf composted treatments may have been less than that of the sludge compost, thereby affecting the absorption/desorption of the soil metals.

Normally, metal uptake by plants increases at lower pH (Elliott 1983). In addition, zinc may adsorb to particles of lime (Tisdale et al. 1985), particularly dolomite, and thus decrease zinc availability in sludge treated soils.

Organic matter may act as a chelating agent of heavy metals. Metals have preferential affinity for organic ligands over inorganic colloids. However at low soil pH, the pH-dependent positive charges in some soils increased in the same way as the pH-dependent negative charges increased with high pH. As a result, when soil pH is relatively low (below pH 6), the adsorption of negatively-charged chelated metals to soil colloids increased. Therefore, plant uptake of heavy metals decreases. On the other hand, when pH increases and more negatively-charged sites appear, the heavy metal cation adsorption increases, but the negatively-charged organo-metallic complexes may remain suspended in solution. The effect of pH on the cation exchange capacity was demonstrated by this study. The lower plant metal uptake from sludge compost-treated soil was related to its high pH (7.1) compared to the relatively lower pH (6.6) of the leaf compost and control (pH 6.4) soils (Preer et al. 1987).

Most studies involving soils with varying cation exchange capacity have also had varying pH and other soil properties which confound the interpretation of the data and often create the difficulty of relating cadmium uptake to any single soil factor. It is reported that some soils in the southeastern U.S. have low cation exchange capacity but high cadmium sorption (Vanderlaan 1981). Studies relating cation exchange capacity in soil to cadmium uptake by plants show conflicting results, because cation exchange capacity does not adequately reflect all soil factors which

influence the uptake of cadmium by plants. These results showed that organic matter in soil does not correspond well with metal uptake by plants. In contrast, increased cation exchange capacity correlated with decreased metal uptake. Haq et al. (1980) found that cadmium concentration in swiss chard was associated with organic matter but not the cation exchange capacity. The effect of organo-metallic complexes is another important metal binding mechanism that is related to organic matter in the soil. However, sludge compost may not provide enough chelating organic materials to form organo-metal complexes.

Appropriateness of soils for amendment with waste containing hazardous substances is dependent on the soil's physical, chemical, and biological properties. This study indicates that soil cation exchange capacity and organic matter can influence heavy metal uptake in selected vegetables, but that these soil properties have complex effects on metal availability. Additional work is necessary to elucidate the effect of organic matter, pH, and cation exchange capacity on chelation of heavy metals.

Important problems remain in establishing the fate of cadmium and zinc and their availability to plants once sludge compost application is discontinued. It would be useful also to shed some light on the processes by which other metals such as calcium and phosphorus may interact with cadmium and zinc in terms of mobility in the soil solution and subsequent plant uptake.

CHAPTER 6

CONCLUSION

Cadmium and zinc levels in soil increased following sludge compost treatment, but applications of leaf compost caused no significant change. Applications of leaf compost only increased soil organic matter. Swiss chard absorbed less zinc and cadmium from sludge compost amended soil than from control soil. Similarly, beet leaves raised in sludge composted soil showed lower zinc and cadmium content. Although sludge compost increases soil heavy metal concentrations, the concomittant increase in cation exchange capacity appears to prevent metal uptake by several vegetables.

REFERENCES

- Albosel, N., and A. Cottenie. 1985. Heavy metal uptake from contaminated soils as affected by peat, lime, and chelates. *Soil Sci. Am. J.* 49: 386-390.
- Anonymous. 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals, p. 1-63. Council for Agricultural Science and Technology. Report No. 64.
- Anonymous. 1980. Effects of sewage sludge on the cadmium and zinc content of crops, p. 7-26. Council for Agricultural Science and Technology. Report No. SW-881.
- Barton, A. F. M. 1979. Resource Recovery and Recycling, p. 99-102. John Wiley and Sons Publishers, New York.
- Black, C. A. 1965. Methods of Soil Analysis - Part 2: Chemical and Microbiological Properties, p. 891-913. American Society of Agronomy, Inc., Madison, Wisconsin.
- Cavallaro, N., and M. B. McBride. 1980. Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. *Soil Sci. Soc. Am. J.* 44:729-732.
- Chaney, R. L. 1973. Crop and food chain effects of toxic elements in sludges and effluents, p. 129-141. *In* Proc. Joint Conf. on Recycling Municipal Sludges and Effluents on Land. Nat. Assoc. State Univ. and Land-Grant Coll., Washington, D. C.
- Chaney, R. L. 1980. Health risks associated with toxic metals in municipal sludge, p. 59-83. *In* G. Bitton, B. L. Damron, G. T. Edds, and J. M. Davidson (ed.), *Sludge - Health risks of land application*. Ann Arbor Science Publishers, Michigan.
- Chaney, R. L. 1982. Heavy metals and toxic materials in waste organics and their effects on agricultural utilization. Washington, D.C.: World Bank. (Unpublished)
- Chaney, R. L., and P. M. Giodano. 1977. Microelements as related to plant deficiencies and toxicities, p. 235-279. *In* Soils for management of organic wastes and wastewaters. Amer. Soc. of Agron., Wisconsin.
- Chubin, R. G., and J. J. Street. 1981. Absorption of cadmium on soil constituents in the presence of complexing ligands. *J. Environ. Qual.* 10:225-228.

- Elliott, H. A. 1983. Adsorption behavior of cadmium in response to soil surface charge. *Soil Science* 136:317-321.
- Elliott, H. A., M. R. Liberati, and C. P. Huang. 1986. Competitive adsorption of heavy metals by soils. *J. Environ. Qual.* 15:214-218.
- Epstein, E., J. M. Taylor, and R. L. Chaney. 1976. Effects of sewage sludge and sludge compost applied to soil on some soil physical and chemical properties. *J. Environ. Qual.* 5:422-426.
- Epstein, E., and R. L. Chaney. 1978. Land disposal of toxic substances and water-related problems. *J. Water Poll. Control Fed.* 50:2037-2047.
- Foy, C. D., R. L. Chaney, and M. C. White. 1978. The physiology of metal toxicity in plants. *Ann. Rev. Plant Physiol.* 29:511-566.
- Gillman, G. P., R. C. Bruce, B. G. Davey, J. M. Kimble, P. L. Searle, and J. O. Skjemstad. 1983. A comparison of methods used for determination of cation exchange capacity. *Commun. in Soil Science Plant Anal.* 14: 1005-1014.
- Haghiri, F. 1974. Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. *J. Environ. Qual.* 3:180-183.
- Haghiri, F. 1976. Release of cadmium from clays and plant uptake of cadmium from soil as affected by potassium and calcium amendments. *J. Environ. Qual.* 5:395-397.
- Haq, A. U., T. E. Bates, and Y. K. Soon. 1980. Comparison of extractants for plant-available zinc, cadmium, nickel and copper in contaminated soils. *Soil Sci. Soc. Amer. J.* 44:772-777.
- Harter, R. D. 1979. Adsorption of copper and lead by Ap and B2 horizons of several northeastern United States soils. *Soil Sci. Soc. Am. J.* 43: 679-683.
- Hinesly, T. D., R. L. Jones, E. L. Ziegler, and J. J. Tyler. 1977. Effects of annual and accumulative applications of sewage sludge on assimilation of zinc and cadmium by corn. *Environ. Sci. & Tech.* 11: 182-188.
- Hornick, S. B., J. J. Murray, and R. L. Chaney. 1980. Overview utilization and composted municipal sludges, p. 15-22. *In* Proceedings of National Conference on municipal and industrial sludge composting and materials handling. Information Transfer Inc., Rockville, Maryland.
- Hubbell, D. S. and G. Staten. 1951. Studies on soil structure. *New Mexico Agricultural Experiment Station Bulletin* 363:51.

- Jacobs, L. W. 1981. Agricultural application of sewage sludge, p. 109-126. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), Sludge and its ultimate disposal. Ann Arbor Science Publishers, Michigan.
- Jenkins, J. C. 1981. Landfilling and renovation with sludges, p. 127-136. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), Sludge and its ultimate disposal. Ann Arbor Science Publishers, Michigan.
- Keeney, D. R., K. W. Lee, and L. M. Walsh. 1975. Guidelines for the application of waste water sludge to agricultural land in Wisconsin, p. 1-36. Technical Bulletin No. 88. Department of Natural Resources, Madison, Wisconsin.
- Kirkham, M. B. 1977. Organic matter and heavy metal uptake. Compost Science (January-February):18-21.
- Korcak, R. F., and D. S. Fanning. 1985. Availability of applied heavy metals as a function of type of soil material and metal source. Soil Science 140:23-34.
- Leeper, G. W. 1978. Managing the Heavy Metals on the Land, p. 10-60. Marcel Dekker, Inc., New York, New York.
- Loehr, R. C. 1981. Environmental impacts of sludge disposal, p. 179-196. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), Sludge and its ultimate disposal. Ann Arbor Science Publishers, Michigan.
- Logan, T. J., and R. Chaney. 1983. Metals, p. 235-326. In A. L. Page, T. L. Gleason, III, J. E. Smith, Jr., I. K. Iskandar, and L. E. Summers (ed.), Proceedings of the 1983 workshop on utilization of municipal wastewater and sludge on land. Riverside, California: University of California.
- Lund, L. J., A. L. Page, and C. O. Nelson. 1976. Movement of heavy metals below sewage disposal ponds. J. Environ. Qual. 5:330-334.
- Mahler, R. J., F. T. Bingham, G. Sposito, and A. L. Page. 1980. Cadmium-enriched sewage sludge application to acid and calcareous soils: Relation between treatment, cadmium in saturation extracts, and cadmium uptake. J. Environ. Qual. 9:359-364.
- Mays, D. A., G. L. Terman, and J. C. Duggan. 1973. Municipal compost: Effects on crop yields and soil properties. J. Environ. Qual. 2: 89-92.
- McBride, M. B., L. D. Tyler, and D. A. Hovde. 1981. Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. Soil Sci. Soc. Am. J. 45:739-744.

- Miller, W. P., D. C. Martens, and L. W. Zelazny. 1985. Effects of manure amendment on soil chemical properties and hydrous oxides. *Soil Sci. Soc. Am. J.* 49:856-861.
- Moore, J. G., Jr. 1981. Sludge: What can be done with it, p. xi-xvii. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), *Sludge and its ultimate disposal*. Ann Arbor Science Publishers, Michigan.
- Nelson, D. W. and L. E. Sommers. 1982. Total carbon, organic carbon, and organic matter, p. 539-577. In *Methods of soil analysis - Part 2: Chemical and microbiological properties*. Amer. Soc. of Agron. Inc., Madison, Wisconsin.
- Niessen, W. R. 1981. The impact of sludge incineration on the environment, p. 197-210. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), *Sludge and its ultimate disposal*. Ann Arbor Science Publishers, Michigan.
- Page, A. L., A. A. Elseewi, and J. P. Martin. 1977. Capacity of soils for hazardous inorganic substances. Paper presented at the National Conference on Composting of Municipal Residues and Sludges, Silver Spring, Maryland, August 23-25, 1977.
- Page, A. L., T. J. Logan, J. A. Ryan. 1987. Land Application of Sludge: Food Chain Implications, p. 67-99. Lewis Publishers, Inc., Chelsea, Michigan.
- Parr, J. F., G. B. Wilson, R. L. Chaney, L. J. Sikora, and C. F. Tester. 1978. Effect of certain chemical and physical factors on the composting process and product quality, p. 130-137. In *Proceedings of the National Conference on Design of Municipal Sludge Compost Facilities*, Chicago, Illinois, 29-31 August 1978. Information Transfer Inc., Rockville, Maryland.
- Purdum, P. W. and S. H. Anderson. 1980. *Environmental Science*, p. 318-331. Merrill Publishing Co., Columbus, Ohio.
- Preer, J., H. Sekhon, A. Abdi, and G. Murchison. 1983. Effect of liming on plant uptake of native soil metals. Abstract presented at the 189th National Meeting of the American Chemical Society, Washington, D.C., August 29-September 2, 1983.
- Preer, J. R., H. S. Sekhon, G. B. Murchison, and L. Smith. 1984. Abstract. Metals uptake and yield improvement in garden vegetables using sludge compost. Amsterdam, Holland: Fifth European Conference on Environmental Pollution, June 11-12, 1984.
- Preer, J. R., G. B. Murchison, Jr., and J. O. Akintoye. 1987. Methods for the analysis of soil and vegetable samples for metals. In *District of Columbia Agricultural Experiment Station Bulletin 2*. Washington, D. C., University of the District of Columbia.

- Rappaport, B. D., D. C. Martens, R. B. Reneau, Jr., and T. W. Simpson. 1987. Metal accumulation in corn and barley grown on a sludge-amended typic ochraqualf. *J. Environ. Qual.* 16:29-33.
- Squires, D. F. 1983. *The Ocean Dumping Quandary: Waste Disposal in the New York Bight*, p. 104-125. State University of New York Press, Albany, New York.
- Street, J. J., W. L. Lindsay, and B. R. Sabey. 1977. Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge. *J. Environ. Qual.* 6:72-77.
- Tisdale, S. L., W. L. Nelson, and J. D. Beaton. 1985. *Soil Fertility and Fertilizers*, p. 382-660. Macmillan Publishing, New York.
- Vanderlaan, G. A. 1981. Federal regulatory considerations in sludge utilization, p. 273-280. In J. A. Borchardt, W. J. Redman, G. E. Jones, and R. T. Sprague (ed.), *Sludge and its ultimate disposal*. Ann Arbor Science Publishers, Michigan.
- Vesilind, P. A., G. C. Hartman, and E. T. Skene. 1976. *Sludge Management and Disposal for the Practicing Engineer*, p. 34-37. Lewis Publishing Inc., Chelsea, Michigan.
- Williams, P. H. 1983. Plant availability of heavy metals in a sludge-treated soil: 1. Effect of sewage sludge and soil pH on the yield and chemical composition of rape. *J. Environ. Qual.* 12:358-365.

APPENDIX A1: Raw data of cation exchange capacity of soil
treated with sludge compost and leaf compost through time.

CEC in meq/100g Soil

<u>Treatment</u>	<u>Plot/1982</u>	<u>Plot/1983</u>	<u>Plot/1984</u>	<u>Plot/1985</u>
Sludge Compost	1 - 37.24	1 - 9.57	1 - 35.90	1 - 35.61
	1 - 41.0	1 - 9.00	1 - 14.35	1 - 33.31
	5 - 60.50	5 - 24.44	5 - 34.14	5 - 36.20
	5 - 40.52	Mean = 14.34	5 - 34.43	5 - 36.52
	Mean = 39.0		Mean = 29.71	Mean = 35.66
Leaf Compost	3 - 37.89	3 - 16.41	3 - 21.85	3 - 26.25
	3 - 8.14	3 - 25.09	6 - 31.01	3 - 25.24
	6 - 26.47	6 - 18.71	6 - 30.60	6 - 31.49
	6 - 21.21	Mean = 20.07	Mean = 27.82	6 - 34.26
	Mean = 25.0			Mean = 29.31
Control	2 - 20.25	2 - 10.85	2 - 18.56	2 - 25.18
	2 - 22.65	2 - 30.37	2 - 13.58	2 - 26.36
	4 - 21.0	4 - 54.42	4 - 25.93	4 - 28.24
	4 - 23.47	Mean = 20.61	Mean = 19.36	4 - 24.08
	Mean = 22.0			Mean = 25.97

APPENDIX A2: Raw data of percent organic matter of soil
treated with sludge compost and leaf compost through time.

Percent Organic Matter in Soil

<u>Treatment</u>	<u>Plot/1982</u>	<u>Plot/1983</u>	<u>Plot/1984</u>	<u>Plot/1985</u>
Sludge Compost	1 - 8.0	1 - 8.0	1 - 12.0	1 - 10.0
	1 - 12.0	1 - 10.0	1 - 13.0	1 - 11.0
	5 - 11.0	5 - 11.0	5 - 13.0	5 - 11.0
	5 - 8.0	Mean = 9.66	5 - 11.0	5 - 11.0
	Mean = 9.75 SE = 1.03	SE = 0.88	Mean = 12.25	Mean = 10.75 SE = 0.25
Leaf Compost	3 - 15.0	3 - 8.0	3 - 12.0	3 - 10.0
	3 - 13.0	3 - 11.0	3 - 12.0	3 - 9.0
	6 - 14.0	6 - 7.0	6 - 11.0	6 - 10.0
	6 - 13.0	Mean = 8.66	6 - 11.0	6 - 11.0
	Mean = 13.75 SE = 0.48	SE = 1.20	Mean = 11.50	Mean = 10.0 SE = 0.40
Control	2 - 9.0	2 - 6.0	2 - 9.0	2 - 8.0
	2 - 8.0	2 - 12.0	2 - 10.0	2 - 8.0
	4 - 10.0	4 - 9.0	4 - 11.0	4 - 10.0
	4 - 10.0	Mean = 9.25	4 - 11.0	4 - 9.0
	Mean = 9.25 SE = 0.48	SE = 0.48	Mean = 10.25	Mean = 8.75 SE = 0.48

APPENDIX A3: Soil pH in plots amended with sludge compost,
leaf compost and control from 1982 through 1985.

<u>Treatment</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
	- - - - - (pH) - - - - -			
Sludge compost	7.5 a* A	6.7 a B	6.7 a B	7.3 a A
Leaf compost	6.4 b AB	6.9 a A	6.3 b B	6.8 b AB
Control	6.4 b AB	6.3 a B	6.1 b B	6.7 b A

* Means followed by the same letter do not differ significantly at the 0.05 level using Duncan's Multiple Range Test. Lower case letters represent comparisons within a column. Capital letters represent comparisons within a row (Preer et al. 1987).